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(54) HYDROGENATION IN A PLATE HEAT EXCHANGER

HYDRIERUNG IN EINEM PLATTENWÄRMETAUSCHER

HYDROGENATION DANS UN ECHANGEUR DE CHALEUR A PLAQUES

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(56) References cited:

EP-A- 0 151 933	**WO-A-92/11500**
FR-A- 946 613	**US-A- 3 634 471**
US-A- 3 809 708	**US-A- 4 510 092**
US-A- 4 719 970	**US-A- 4 871 485**

- **DATABASE WPI Week 9049, Derwent Publications Ltd., London, GB; AN 90-364587 & JP,A,2 261 897 (SNOW BRAND MILK PRODUCTS) 24 October 1990 cited in the application**

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Description

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to hydrogenation of fatty materials in a plate heat exchanger. Specifically, it relates to processes for lightly hydrogenating unsaturated fatty materials like fatty acids, fatty esters, etc., while maintaining a favorable trans-/cis-isomer ratio and/or hydrogenating to a very low Iodine Value.

Description of Related Art

Hydrogenation of fatty materials is well known, having been described in U.S. Pat. Nos.: 3,073,380, Palmason; 3,634,471, Kehse; 3,809,708, Minor; 4,584,139, Gray et al.; and 4,871,485, Rivers; Japanese Pat. Appln. 02/261,897; and Soviet Union Appln. 1,142,505. The use of a plate and frame heat exchanger for hydrogenation is disclosed in U. S. Pat. No. 3,809,708.

SUMMARY OF THE INVENTION

This invention relates to a process for hydrogenating unsaturated fatty acids and/or their esters in a heat exchanger of the type generally referred to as a "plate" heat exchanger, preferably one that has a solid outer shell construction, e.g., welded, so as to provide a vessel which can withstand high pressures, e.g., more than about 1 034 250 Pa (150 psig), the vessel having an internal configuration to provide high shear mixing under normal flow rates, and the process being run under a pressure of more than about 1 034 250 Pa (150 psig), preferably from about 1 034 250 (150) to about 3 447 500 Pa (500 psig), more preferably from about 2 068 500 (300) to about 2 758 000 (400 psig), the combination of high shear mixing and high pressure being sufficient to effect essentially complete reaction of the hydrogen used in the process, so that the amount of hydrogen used determines the degree of hydrogenation and the temperature can be lowered during "touch hardening" to avoid formation of the trans- isomer.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention improves the existing art processes by increasing the pressure and/or shear used in the hydrogenation of fatty materials (also referred to herein as "fatty reactants" and/or "feedstock") while maintaining the advantage of superior temperature control that a plate heat exchanger provides. The common heat exchangers, of the type used in U.S. Pat. No. 3,809,708, are not suitable for optimum use, since they rely upon compression and a series of seals to maintain pressure. Preferably the heat exchanger is one that has a solid outer shell, e.g., one like those sold by Packinox of Louveciennes, France under the trade name Packinox, and by Karbate Vicarb, Inc. under the trade name Compabloc, the said heat exchangers being modified to have ratios of surface area to volume (S/V) of at least about 75, preferably from about 75 to about 300, more preferably from about 150 to about 300. The heat exchanger should have the ability to operate continuously and safely under a pressure of from about 1 034 250 (150) to about 3 447 500 Pa (500 psig), preferably from about 2 068 500 (300) to about 3 447 500 (500 psig), more preferably from about 2 068 500 (300) to about 2 758 000 Pa (400 psig). The higher pressures of hydrogen are preferred to maximize the amount of hydrogen that is dissolved in the fatty reactants, especially under conditions of low temperature.

The plate heat exchanger (hydrogenation reactor), may have inlets for the hydrogen gas at more than one place to allow introduction of the hydrogen gas as the dissolved gas is used up. This permits the reaction to continue without the necessity of having excess gas present in the initial stages when it would be present as a gas and interrupt the transfer of heat. This is desirable when one is interested in fully hydrogenating a feedstock. The heat exchanger is primarily used to remove heat as it is produced by the reaction and thereby maintain conditions where a minimum of undesirable by-products are formed and/or minimal conversion of cis- to trans- isomers occurs. Isomer conversion is increased by high temperature and slow reactions.

The heat exchanger should have the capability of removing the heat of the reaction as it occurs to maintain the temperature within the range of from about 120° to about 240°C, preferably from about 120° to about 180°C, more preferably from about 120° to about 150°C. This temperature range is optimum for slightly reducing the Iodine Value (IV) of the fatty reactant while minimizing formation of the trans-isomer of unsaturated fatty acids. It is recognized that when the IV is lowered to very low levels, there is very little unsaturation and therefore less need to be concerned about isomers.

The heat exchanger, in operation, should provide high shear stress, which is directly related to pressure drop per unit of the flow path length. Preferably the pressure drop per unit length is from about 4 524, 2782 (0.2) to about 45

242, 782 Pa/m (2.0 psig/ft.), more preferably from about 11 310, 695 (0.5) to about 22 621, 39 Pa/m (1 psig/ft).

The combination of high pressure, high shear, and/or low temperature provide fast hydrogenation at mild conditions, e.g., a combination of time and temperature, that permit one to provide high production rates and/or hydrogenated fatty materials that have excellent color, heat stability, and/or odor, even for materials that are almost fully, or fully, hydrogenated.

Preferred reactors herein are those which have: a solid outer shell; an internal structure that mimimizes by-passing of the plates; the cabability of maintaining an internal pressure during the reaction of from about 1 034 250 (150) to about 3 447 500 Pa (500 psig), preferably from about 2 068 500 (300) to about 3 447 500 Pa (500 psig); a ratio of internal surface to internal volume (S/V) of from about 75 to about 300, preferably from about 150 to about 300, more preferably from about 200 to about 300; and are fabricated from material that is resistant to becoming brittle when in contact with hydrogen and/or the fatty reactant, as defined hereinafter.

Fatty Reactants

The fatty reactants include any of the fatty acids containing unsaturation. Typically, the fatty acids contain from about 8 to about 26 carbon atoms, preferably from about 14 to about 22 carbon atoms, more preferably from about 16 to about 18 carbon atoms. The fatty reactants also include the esters of the above fatty acids, e.g., their methyl and ethyl esters and the mono-, di-, and tri- glycerides, and monohydroxy alcohols containing from about 8 to about 24, preferably from about 14 to about 22 carbon atoms. The most preferred fatty reactants are the methyl esters.

The fatty acids that can be hydrogenated include: soybean, palm oil, erucic, canola, coconut, palm oil stearine, tallow, etc. The corresponding methyl esters are also desirable reactants.

Additional fatty reactants include the corresponding ethyl esters and the corresponding mono-, di-, and tri- glycerides.

The IV of the starting fatty material is typically at least about 5, preferably at least about 30, and typically from about 30 to about 150, preferably from about 30 to about 120. The IV is typically lowered by from about 2 to about 15, preferably from about 5 to about 10 for "touch hardening" and to less than about 2, preferably less than about 1, for complete hardening. When the fatty material is touch hardened, the trans-isomers are preferably increased by less than about 15%, more preferably less than about 5%.

Hydrogen

The hydrogen gas that is used in the reaction should be free from any contaminants that will interfere with the reaction. Specifically the hydrogen should be free of moisture. It is desirable to use as little as possible of the hydrogen gas to minimize separation and to maximize safety. Since the reaction herein is so efficient, the excess of hydrogen over the desired level of hydrogenation is typically no more than about 25%, preferably no more than about 10%, more preferably no more than about 5%.

The Catalyst

Any of the normal hydrogenation catalysts can be used. The catalyst can be, and typically is used in finely divided form, preferably having a particle size of from about 0.5 to about 20 microns, preferably from about 1 to about 10 microns, more preferably from about 4 to about 5 microns. The small catalyst size is preferred since the catalyst is suspended in the fatty reactant and the smaller sizes are more stably suspended.

The catalysts include the nickel catalysts, typically Raney nickel catalysts, either supported, or not supported. Other catalysts include platinum and palladium catalysts, again, either supported, or not supported. The catalyst can be either recycled, or not, as the process proceeds. Preferred catalysts include: nickel, copper, palladium, platinum, and cobalt catalysts. Mixtures of the above catalysts can also be used.

The level of the catalyst can be kept low, typically from about 0.05% to about 1%, preferably from about 0.02% to about 0.5%.

In the following Examples, and in the specification, all percentages, parts, and ratios are by weight and all figures are approximations unless otherwise specified.

EXAMPLES

In the following runs, the plate and frame heat exchangers have the following physical dimensions:

Plate and Frame Heat Exchangers		
	Runs 1-6	Runs 7-8
Plate Heat Exchanger Type	Gasketed	Welded
No. of Process Channels	24	8
No. of Channels/Pass	1	8
Plate Gap (mm)	2.4	2.5
Plate Width (mm)	102	102
Plate Length (mm)	357	10668
Chevron Angle (from vertical)	60	60
	Run 9	Run 10
Plate Heat Exchanger Type	Welded	Gasketed
No. of Process Channels	100	100
No. of Channels/Pass	2	2
Plate Gap (mm)	5.0	3.0
Plate Width (mm)	200	326
Plate Length (mm)	200	945
Chevron Angle (from vertical)	45	60

The fatty reactants in the runs are tallow fatty acids which have the following initial Iodine Values and trans fatty acid contents.

	Runs 1-4	Runs 5-6	Runs 7-10
Iodine Value	52.2	52.0	48.3
Trans Acids	5.1	3.8	4.5

The operating conditions and results in the runs are as follows:

Operating Conditions and Results

Run	Temp. (°C) (°F)	Pressure* (Pa) (psig)	FA Flow (kg/s) (lb/hr)	H_2 Flow (kg/s) (lb/hr)
1	221 (430)	517 125(75)	$7,56\ 10^{-3}$(60)	$419\ 10^{-5}$(.095)
2	221 (430)	517 125(75)	$7,56\ 10^{-3}$(60)	$8,5\ 10^{-6}$(.068)
3	171 (340)	551 600(80)	$7,56\ 10^{-3}$(60)	$1,19\ 10^{-5}$(.095)
4	171 (340)	517 125(75)	$7,56\ 10^{-3}$(60)	$6,9\ 10^{-6}$(.055)
5	146 (295)	1 034 250(150)	$7,56\ 10^{-3}$(60)	$6,3\ 10^{-6}$(.050)
6	146 (295)	1 034 250(150)	$7,56\ 10^{-3}$(60)	$3,1\ 10^{-6}$(.025)
7	121 (250)	1 723 750(250)	0,126 (1000)	$1,801\ 10^{-4}$(1.43)
8	213 (415)	1 723 750(250)	$8,82\ 10^{-2}$(700)	$4,12\ 10^{-4}$(3.27)
9	213 (415)	1 723 750(250)	0,1638(1300)	$7,799\ 10^{-4}$(6.19)
10	210 (410)	1 034 250(150)	$8,82\ 10^{-2}$(700)	$4,573\ 10^{-4}$(3.63)

*Inlet Pressure

Operating Conditions and Results (Continued)

Run	Ni (Wt.%)	Iodine Value	% Trans Acids
1	.05	39.4	20.0
2	.30	41.6	16.0
3	.50	38.4	13.1
4	.10	45.4	10.5
5	.05	48.8	7.6
6	.05	45.0	8.0
7	.10	37.1	6.7
8	.15	1.8	-
9	.15	5.0	-
10	.15	2.3	-

As can be seen from the above, low levels of catalyst can be used (1 vs. 2 or 3) with essentially equivalent results. Also, the use of lower temperatures and higher pressures (1-4 vs. 5-7) reduces trans- fatty acid content while still reducing the Iodine Value. It is also seen that the output can be increased by simply increasing the reactant throughputs and reactor size (6 vs. 7) and that the level of hydrogenation can be increased by simply increasing the amount of hydrogen relative to the fatty reactant (3 vs. 4 and 7 vs. 8-10). These results could not have been predicted in advance.

Claims

1. The process of hydrogenating a fatty material in a plate and frame heat exchanger having a ratio of surface to volume of at least about 75, preferably from about 75 to about 300, more preferably from about 150 to about 300, at a pressure of at least 1 034 250 Pa (150 psig), preferably from about 1 034 250 Pa (150 psig) to about 3 447 500 Pa (500 psig), more preferably from about 2 068 500 Pa (300 psig) to about 2 758 000 Pa (400 psig), the pressure drop per meter being at least about 4 524, 2782 Pa, preferably from about 4 524,2782 to about 45 242,782 Pa, and, preferably, wherein the temperature is maintained within from about 120°C to about 240°C, more preferably from about 120°C to about 180°C, and even more preferably from about 120°C to about 150°C.

2. The process of Claim 1 wherein said pressure drop per meter is from about 11 310,695 to about 22 621,39 Pa.

3. The process of Claim 1 or Claim 2 wherein said fatty material is selected from the group consisting of:

   A. Fatty acids containing from about 8 to about 26 carbon atoms and having an Iodine Value of more than about 5;
   B. Esters of said fatty acids; and
   C. Fatty alcohols containing from about 8 to about 24 carbon atoms and having an Iodine Value of more than about 5.

4. The process of Claim 3 wherein said Iodine Value is reduced by at least about 5 while increasing the percentage of trans-isomers by no more than about 15% of the original value.

5. The process of Claim 3 or Claim 4 wherein said fatty material is a methyl ester of said fatty acids.

6. The process of Claim 3 or Claim 4 wherein said fatty material is a fatty acid.

7. The process of any of Claims 3-6 wherein the Iodine Value of said fatty material is reduced to less than about 2.

8. The process of any of the above Claims wherein said heat exchanger has a solid shell.

Patentansprüche

1. Verfahren zum Hydrieren eines Fettmaterials in einem Platten- und Rahmenwärmetauscher mit einem Oberflächen-zu-Volumen-Verhältnis von zumindest etwa 75, bevorzugt etwa 75 bis etwa 300, noch stärker bevorzugt etwa 150 bis etwa 300, bei einem Druck von zumindest 1034250 Pa (150 psig), bevorzugt etwa 1034250 Pa (150 psig) bis etwa 3447500 Pa (500 psig), noch stärker bevorzugt etwa 2068500 Pa (300 psig) bis etwa 2758000 Pa (400 psig), wobei der Druckabfall pro Meter zumindest etwa 4524,2782 Pa, bevorzugt etwa 4524,2782 bis etwa 45242,782 Pa beträgt, und wobei bevorzugt die Temperatur in einem Bereich von etwa 120°C bis etwa 240°C, stärker bevorzugt von etwa 120°C bis etwa 180°C, und noch stärker bevorzugt von etwa 120° bis etwa 150°C gehalten wird.

2. Verfahren nach Anspruch 1, bei welchem der Druckabfall pro Meter etwa 11310,695 bis etwa 22621,39 Pa beträgt.

3. Verfahren nach Anspruch 1 oder 2, bei welchem das Fettmaterial aus der Gruppe bestehend aus:

   A. Fettsäuren mit etwa 8 bis etwa 26 Kohlenstoffatomen und einer Jodzahl von mehr als etwa 5;
   B. Estern der genannten Fettsäuren; und
   C. Fettalkoholen mit etwa 8 bis etwa 24 Kohlenstoffatomen und einer Jodzahl von mehr als etwa 5 gewählt ist.

4. Verfahren nach Anspruch 3, bei welchem die Jodzahl um zumindest etwa 5 reduziert wird, während der Prozentsatz an Transisomeren um nicht mehr als etwa 15% des ursprünglichen Wertes erhöht wird.

5. Verfahren nach Anspruch 3 oder 4, bei welchem das Fettmaterial ein Methylester der genannten Fettsäuren ist.

6. Verfahren nach Anspruch 3 oder 4, bei welchem das Fettmaterial eine Fettsäure ist.

7. Verfahren nach einem der Ansprüche 3 bis 6, bei welcher die Jodzahl des Fettmaterials auf weniger als etwa 2 reduziert wird.

8. Verfahren nach einem der vorangehenden Ansprüche, bei welchem der Wärmetauscher ein festes Gehäuse aufweist.

Revendications

1. Procédé d'hydrogénation d'une matière grasse dans un échangeur de chaleur à cadres et à plateaux ayant un rapport surface sur volume d'au moins environ 75, de préférence d'environ 75 à environ 300, de préférence encore d'environ 150 à environ 300, à une pression d'au moins 1 034 250 Pa (150 psig), de préférence d'environ 1 034 250 Pa (150 psig) à environ 3 447 500 Pa (500 psig), de préférence encore d'environ 2 068 500 Pa (300 psig) à environ 2 758 000 Pa (400 psig), la chute de pression par mètre étant d'au moins environ 4 524,2782 Pa, de préférence d'environ 4 524,2782 à environ 45 242,782 Pa, et de préférence, dans lequel la température est maintenue dans une gamme d'environ 120°C à environ 240°C, de préférence d'environ 120°C à environ 180°C, et de préférence encore d'environ 120°C à environ 150°C.

2. Procédé selon la revendication 1, dans lequel ladite chute de pression par mètre est d'environ 11 310,695 à environ 22 621,39 Pa.

3. Procédé selon la revendication 1 ou la revendication 2, dans lequel ladite matière grasse est choisie dans le groupe composé :

   A. d'acides gras contenant d'environ 8 à environ 26 atomes de carbone et ayant un indice d'iode supérieur à environ 5;
   B. d'esters desdits acides gras; et
   C. d'alcools gras contenant d'environ 8 à environ 24 atomes de carbones et ayant un indice d'iode supérieur à environ 5.

4. Procédé selon la revendication 3, dans lequel ledit indice d'iode est réduit d'au moins environ 5, tandis que le pourcentage d'isomères trans augmente de pas plus d'environ 15% de la valeur d'origine.

5. Procédé selon la revendication 3 ou la revendication 4, dans lequel ladite matière grasse est un ester méthylique desdits acides gras.

6. Procédé selon la revendication 3 ou la revendication 4, dans lequel ladite matière grasse est un acide gras.

7. Procédé selon l'une quelconque des revendications 3 à 6, dans lequel l'indice d'iode de ladite matière grasse est réduit à moins d'environ 2.

8. Procédé selon l'une quelconque des revendications ci-dessus, dans lequel ledit échangeur de chaleur possède une enveloppe pleine.